SYNTHESIS AND CHARACTERIZATION OF Al_2O_3-CeO_2 NANO-COMPOSITES FOR REMOVAL OF ORGANIC DYE MOLECULES

A Dissertation

Submitted in partial fulfilment

FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

Affiliated to

Deemed University

By

SUSMITA KUMARI SAHU

Under the Guidance of

Dr. G. Hota

DEPARTMENT OF CHEMISTRY

NATIONAL INSTITUTE OF TECHNOLOGY,

ROURKELA, 769008

National Institute of Technology, Rourkela
Rourkela -769008, INDIA

Dr. G. Hota

Department of Chemistry

National Institute of Technology, Rourkela

Rourkela 769 008

CERTIFICATE

This is to satisfy that the thesis entitled "***SYNTHESIS AND CHARACTERIZATION OF Al_2O_3-CeO_2 NANO-COMPOSITES FOR REMOVAL OF ORGANIC DYE MOLECULES***" being submitted by **Ms. Susmita Kumari Sahu** (Roll No. 409CY2028) for the partial fulfilment of the requirements for the award of M.Sc. degree in Chemistry at the National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University or Institute for the award of a degree or diploma.

N.I.T Rourkela Supervisor

05 May'2011 **Dr.Garudadhwaj Hota**

DECLARATION

I, **Susmita Kumari Sahu** hereby declare that this project report entitled **"*SYNTHESIS AND CHARACTERIZATION OF Al_2O_3-CeO_2 NANO-COMPOSITES FOR REMOVAL OF ORGANIC DYE MOLECULES*"** is the original work carried out by me under the supervision of **Prof. G. Hota**, Department of Chemistry, National Institute of Technology Rourkela (NITR), Rourkela and the present work or any other part thereof has not been presented to any other University or Institution for the award of any other degree regarding to my belief.

May 5, 2011 Susmita Kumari Sahu

ACKNOWLEDGEMENT

I wish to express my profound appreciation to my supervisors, Prof. G. Hota, Department of Chemistry, National Institute of Technology, Rourkela for his advice, support, and encouragement. I truly cannot imagine myself accomplishing this work without his guidance.

I sincerely thank our H.O.D. Dr. B. G. Mishra for giving us permission to carry out our research work anytime, without which I hardly can complete my project work.

I would like to express my sincere gratitude to Ms. Abhipsa Mohapatra (Research Scholar) and my lab mates for sharing their knowledge and offering their help and words of cheer. These will be remembered in my heart.

I must acknowledge people who once offered some help and concern to my study.

Finally, I am very grateful to my family members. Without their love, understanding, sacrifice, patience, support and confidence, I would never have achieved this goal.

DATE: 05.05.2011 SUSMITA KUMARI SAHU

ABSTRACT

The Al_2O_3-CeO_2 mixed nanocomposites were successfully prepared by using combustion synthetic process. The resulting nanocomposite has been characterized by using XRD, SEM and SEM-EDAX analytical techniques. The X-Ray diffraction (XRD) analysis studies clearly suggest the formation of alumina-ceria mixed composite. The SEM analysis indicates the formation of porous and flakes like morphology in mixed composite nanomaterials. The SEM-EDAX (Element detection X-Ray analysis) results indicate the presence of Al, Ce & O elements in the alumina/ceria mixed composites. The results of combustion synthesis elucidate that the fuel to oxidizer ratio is the most effective factor for the formation and surface morphology of mixed nanocomposite. The synthesized Al_2O_3-CeO_2 mixed nanocomposite has been used for the adsorption studies of Congo red and Methyl orange dye by batch experiments. It is found from the adsorption studies that the removal percentage of Congo red is much better then methyl orange. CeO_2 particles are good adsorbent materials for removal of Congo-red and Methyl Orange dyes as compare to the pure alumina nanopowder. However, the adsorption capacity of alumina can be improve by doping with CeO_2.

Keywords: Al_2O_3-CeO_2 composite, Combustion Synthesis, Congo red, Methyl Orange

INTRODUCTION

Nanotechnology is a field of applied science focused on the design, synthesis, characterization and application of materials and devices on the nanoscale. Nanotechnology relying on the manipulation, control and integration of atoms and molecules to form materials, structures, components, devices, and systems at the nanoscale, is the application of nanoscience, especially to industrial and commercial objectives. In particular that nanotechnology consists of materials with small dimensions, remarkable properties, and great application potential.

Nanocomposite materials which exploded in recent research in material inorganic chemistry processes not only represent a creative alternative to design new materials and compounds for modern/small scale research, but also their improved or usual features allow the development of innovative industrial applications. Nanocomposites have attracted tremendous attention due to their potential applications in biomedical, catalytic, separation, chemical sensing, fuel cell, capacitor, micro-fabrication, tribological, resonant coupling, and high flux gas transport.

Alumina is a porous material and widely used as a catalyst. Its properties differ substantially from those of other porous material. Alumina is extensively used in chemical applications due to its high specific surface and is much cleared pore structure. Ceria (CeO_2) is one of the oxides which are mostly used to progress the performance of alumina. CeO_2 is a multifunctional rare earth oxide with various physics and chemical properties. Ceria can affect the structural stability and thermal stability of alumina, the degree of dispersion of a metal catalyst supported on an alumina catalyst carrier. Thus CeO_2-Al_2O_3 is used in many ways of catalytic process.

The present study builds on several area of research comprising methyl red dye degradation; malachite green dye removal using surfactant-modified alumina; Sn/Nb_2O_5 composite for methyl blue dye removing; Azo dye removal using $CuFe_2O_4$; Dye removal using metal doped alumina catalysts; Fe_2O_3-CeO_2-TiO_2/γ-Al_2O_3 as catalyst for methyl orange azo dye; porous CeO_2 nanowires/nanoarrays CeO_2-Al_2O_3 composite for high temperature catalytic process.

Gupta et al. (2006) in their study they have used untreated TiO_2 and Ag^+ doped TiO_2 for photo catalytic degradation of mixture of crystal violet and methyl red dye under UV irradiation. Das et al. (2009) have tested surfactant-modified alumina adsorbent for malachite green removal from water environment. More recently, Cantao et al. (2010) have reported on the removal of methyl blue using Sn/Nb_2O_5 composite. Lu et al. (2010), have presented a template and surfactant-free electrochemical method for the fabrication of hierarchical porous CeO_2 NWs have and NWAs, 50-200 nm of diameters and various micrometers of lengths of porous NWs/NWAs have used in removing of congo red in treatment of wastewater. Gao et al. (2009) have prepared and characterized of spherical CeO_2-Al_2O_3 composites supporting for high temperature catalytic processes.

In this present research we have synthesized Al_2O_3-CeO_2 composites nanomaterials by combustion synthesis method. Al_2O_3-CeO_2 composites are characterized and are used as adsorbent materials for removal of organic dye molecule from aqueous system.

EXPERIMENT DETAILS

MATERIALS

The following chemicals were used for the synthesis of Al_2O_3-CeO_2 nanocomposites in all our experiment without further purifications. They are Al $(NO_3)_3$•$9H_2O$ (purchased from S. D. Fine chemical Ltd. India, Ce $(NO_3)_3$•$6H_2O$ (Loba Chemie. Ltd. India) and Urea (NH_2CONH_2) obtained from Loba Chemie. India. Double distilled water was used during the whole experiment.

METHODS

Al_2O_3-CeO_2 composites were prepared by combustion synthesis method. Al_2O_3-CeO_2 nanocomposites were synthesized by taking the oxidizers (Al $(NO_3)_3$·$9H_2O$;Ce $(NO_3)_3$·$6H_2O$) and fuel(urea) ratio at 1:1. However we have taken the ratio between Al $(NO_3)_3$·$9H_2O$ and Ce$(NO_3)_3$·$6H_2O$ in different manner such as 1:1 and 2:8. For this synthesis we have mixed the required amount of Al $(NO_3)_3$·$9H_2O$, Ce $(NO_3)_3$·$6H_2O$ and urea (NH_2CONH_2) with continuous stirring and the ration of oxidizer fuel was maintained at 1:1. Thus 5 ml of doubled distilled water added to the mixed solution and stirring until complete transparent solution appears. Then it was heated in a preheated furnace for half an hour at 400°C to obtain the desire mixed nanocomposite sample.

We have also varied the molar ratio of aluminium nitrate and cerium nitrate precursors to prepared different molar ratio of Al_2O_3 - CeO_2 nanocomposites by combustion synthetic method.

ADSORPTION STUDIES

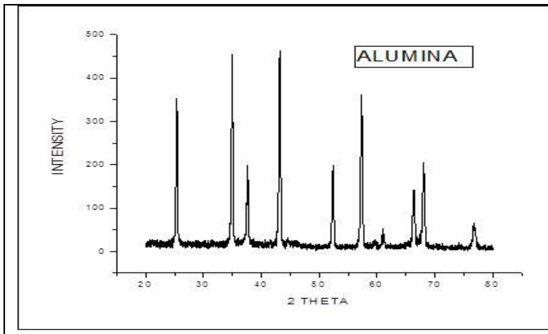
Adsorption measurements for selected organic pollutants were performed by batch experiments adding 0.1 gm of prepared sample into 20 ml of congo red ($C_{32}H_{22}N_6O_6S_2Na_2$) solution (100 mgL-1) and 20 ml of methyl orange solution ($100mL^{-1}$) under stirring condition. This procedure continued at different time intervals, at different pH and at different dose/amount of sample. After the appropriate time of stirring, the solution was filtered by F-40 filter paper, and finally analyzed by UV-Visible spectrophotometer (UV- 2450).

RESULTS AND DISCUSSIONS

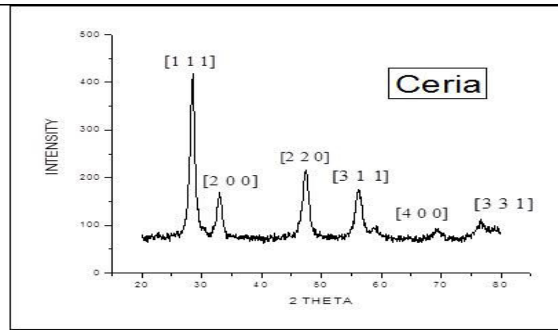
Aluminium oxide, Cerium oxide and Alumina/Ceria mixed nanocomposite prepared by combustion synthesis method are characterized by XRD Analysis, SEM, and EDAX Analysis.

XRD ANALYSIS

XRD of Al_2O_3 represents the X-Ray diffraction spectra of alumina and ceria particles prepared by combustion synthesis method.



XRD of Al_2O_3

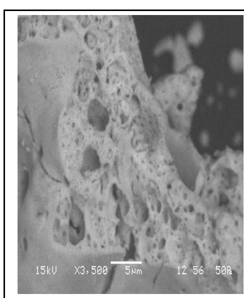


XRD of CeO_2

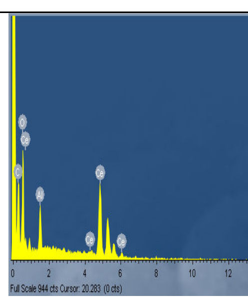
The 2θ value of alumina sample was found to match with JCPDS - 42-1468 confirming the formation of alumina. The 2θ value of ceria sample was found to match with JCPDS - 81-0792 confirming the formation of ceria. X-Ray diffraction pattern also confirms the formation of alumina-ceria mixed sample.

SEM ANALYSIS

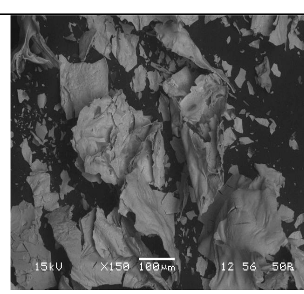
The surface morphology of alumina, ceria and alumina ceria mixed sample particles have been studied by scanning electron microscopy method. The below images represent SEM and EDAX images of Al_2O_3, CeO_2 and mixed sample (AlCe2:8 and AlCe1:1). The EDAX analysis of alumina ceria nanocomposite suggests the presence of Al,O,Ce in the composite. The pore structure and flake like structure found in mixed sample.



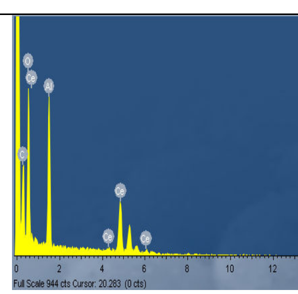
SEM images of AlCe (1:1) sample



EDAX of AlCe (1:1) sample



SEM images of AlCe (2:8) sample



EDAX of AlCe (2:8) sample

Here we used alumina, ceria and mixed samples for removal of congo red and methyl orange dye from solutions. The adsorption of congo red is more in case of ceria and less in alumina. In case of mixed samples, in which amount of cerium nitrate is more i.e. AlCe2:8, the adsorption is slight increase in comparison to AlCe1:1 sample.

DYE REMOVAL

Dye removal efficiency (%R) in according to time variation (min.) was calculated from UV-Vis absorbance spectra. Here we observed that the dye removal efficiency is higher in case of pure (CeO_2) ceria nanopowder i.e. about 100%. The mixed sample AlCe 2:8 show the removal efficiency is in between 80-90%. However, incase of pure alumina (Al_2O_3) nanopowder the removal efficiency is very less. The congo red removal efficiency of the mixed composite increases with increasing is ceria doping to alumina materials. It is also observed that methyl orange dye removal efficiency in ceria is about 95%. But in other two mixed sample there is irregular dye removal efficiency in according to time variation, the range is about 32-65%. It is seen that lower pH gives high value of dye removal efficiency. In both cases pH 6 is the optimum value adsorption. After pH 6, the percentage removal efficiency maintains an equilibrium value. The graph of %R in different sample amount (sample is AlCe2:8) shows, as the amount of sample increases, the dye removal efficiency is also increases. We have varied the adsorbent doses from 0.025, to 0.1 gm for adsorption studies of both Congo red and Methyl orange dye. It is seen that the adsorption capacity of Al_2O_3-CeO_2 nanocomposite adsorbent materials is more in case of Congo red than that of methyl orange dye.

CONCLUSION

The following are some points for conclusion derived from the study.

- We have successfully prepared Al_2O_3-CeO_2 nanocomposite materials using combustion synthesis method.
- XRD studies confirmed the formation of nanocomposite materials.
- SEM micrographs suggest the ceria particles are spherical in shape and the Al_2O_3-CeO_2 nanocomposites are of flake like morphology with porous structure.
- Adsorption studies indicates that CeO_2 particles are good adsorbent materials for removal of Congo-red and Methyl Orange dyes and the adsorption capacity of alumina can be improve by doping with CeO_2.

FUTURE WORK

- This work can be extended by removing other dyes using Al_2O_3-CeO_2 hybrid nanocomposite.
- To study adsorption performance of those dyes and comparison between them.

REFERENCES

1. Hornyak, G. L. et al. *Introduction to Nanoscience and Nanotechnology*, CRC Press: Boca Raton, **2009**.

2. Babloo. Properties of nanomaterials, Study material, University of Delaware, Newark.

3. Kathleen Hickman; "Nanomaterials: It's a Small, Small World: Review article from Proquest, **2002**

4. Twardowski, Thomas E. *Introduction to Nanocomposite Materials: Properties, Processing, Characterization*, DESTech Publications: Lancaster, **2007**.

5. Mancini, L. H. And Esposito, C. L. *Nanocomposites: Preparation, Properties, And Performance*, Nova Science Publishers: New York, **2008**.

6. Camargo, P. H. C.; Satyanarayana, K. G. ; Wypych, F.; "Nanocomposites: Synthesis, Structure, Properties and New Application Opportunities", *Materials Research*, 12, **2009**, 1-39.

7. Patil , P. P.; Patil, D.; "Conducting polymer/Metal oxide nanocomposites in sensor applications": Coference paper presented at First International conference on composites and nanocomposites (ICNC 2011), January 7-9, **2011** held at Kottayam Kerala, India

8. Acquarulo, L. A.; O'Neil, C. J.; Godaire, R. E.; "Nanocomposite for Medical Applications": Paper on nanocomposite of PolyMedex Discovery Group, **2005**

9. Gupta, A. K.; Pal, Anjali; Sahoo, C.; "Photocatalytic degradation of a mixture of Crystal Violet (Basic Violet 3) and Methyl Red dye in aqueous suspensions using AgC doped TiO_2", *Dyes and Pigments*, 69, **2006**, 224-232.

10. Das, A. K. et al.; "Surfactant-modified alumina: An efficient adsorbent for malachite green removal from water environment", *Journal of Environmental Science and Health Part A,* 44, **2009**, 896-905.

11. Lu, Xi-hong et al.; "Porous CeO_2 nanowires/nanowore arrays: electrochemical synthesis and application in water treatment", *Journals of Materials Chemistry, 20,* **2010**, 7118-7122.

12. Cantao, Fabiane de Oliveira et al.; "Utilization Sn/Nb_2O_5 composite for the removal of methylene blue", *Quim. Nova,* 33, **2010**, 528-531.

13. Gao, Chao et al.; "Preparation and characterization of spherical mesoporous CeO_2–Al_2O_3 composites with high thermal stability", *Ind. Eng. Chem.*, 48, **2009**, 6544-6549.